

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100

(43) International Publication Date  
1 February 2001 (01.02.2001)

PCT

(10) International Publication Number  
WO 01/06997 A1

- (51) International Patent Classification<sup>7</sup>: A61K 7/06 (74) Agent: THACKER, Michael, Anthony; The Boots Company plc, Group Patents Dept., Building D31, 1 Thane Road West, Nottingham, Nottinghamshire NG2 3AA (GB).
- (21) International Application Number: PCT/EP00/07196
- (22) International Filing Date: 26 July 2000 (26.07.2000) (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
9917729.7 28 July 1999 (28.07.1999) GB
- (71) Applicant (*for all designated States except US*): THE BOOTS COMPANY PLC [GB/GB]; 1 Thane Road West, Nottingham, Nottinghamshire NG2 3AA (GB).
- (72) Inventors; and
- (75) Inventors/Applicants (*for US only*): CRAIG, Ailsa, Helen, Louise [GB/GB]; The Boots Company plc, 1 Thane Road West, Nottingham, Nottinghamshire NG2 3AA (GB). GALLEY, Edward [GB/GB]; The Boots Company plc, 1 Thane Road West, Nottingham, Nottinghamshire NG2 3AA (GB). LONG, Stewart, Paul [GB/GB]; The Boots Company plc, 1 Thane Road West, Nottingham, Nottinghamshire NG2 3AA (GB). PYKETT, Melanie, Ann [GB/GB]; The Boots Company plc, 1 Thane Road West, Nottingham, Nottinghamshire NG2 3AA (GB).
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:
- With international search report.
  - Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: HAIR CARE COMPOSITION

(57) Abstract: Hair care compositions containing a synergistic mixture of three anti-free-radical agents selected from (a) ascorbic acid, its salts and esters; (b) tocopherol and its esters, such as tocopherol acetate; and (c) herbal extracts selected from *morus alba*, *origanum vulgare*, *panax ginseng*, *rosmarinus officinalis*, *camellia sinensis* and grape seed extract in a suitable diluent or carrier. Preferred synergistic mixtures are *Organum vulgare*, sodium ascorbyl phosphate and *morus alba*. *Organum vulgare*, sodium ascorbyl phosphate and *panax ginseng*. *Panax ginseng*, *morus alba* and *Organum vulgare*. Sodium ascorbyl phosphate, *morus alba* and *camellia sinensis*. Sodium ascorbyl phosphate, *morus alba* and grape seed *Organum vulgare*, *panax ginseng* and *rosmarinus officinalis*.

WO 01/06997 A1

10/027,435  
Jik lpf

- 1 -

### HAIR CARE COMPOSITION

5 The present invention relates to hair care compositions having protecting and conditioning properties and to methods of using such compositions to treat hair.

10 The hair is exposed to a number of environmental challenges. Such exposure can generate free-radicals, especially on exposure to sunlight and/or heat, and presence of high concentrations of free radicals is generally seen as undesirable in a toiletries composition to be used on the hair. Free radicals, which are generated by factors such as UV radiation (present in sunlight), heat and/or by chemical reaction, are implicated in the process of damage to hair, reduction in shine, poor feel, and fading of hair colour.

15 There are a number of haircare compositions, commercially available, which seek to minimise the damage to the hair by the inclusion of certain agents. In particular materials such as vitamins and herbal extracts have widely been known to reduce the formation of free-radicals. However to achieve good efficiency high levels of these materials have to be used and this can result in dark aesthetically unpleasing products that can stain the hair

20

The hair care compositions of the present invention have been shown to protect the hair more effectively from free radicals and are cosmetically and aesthetically more suitable than known hair care compositions. Therefore the hair care compositions of the present invention may be used to provide improved protection against damage to hair caused by exposure to factors such as sunlight, environmental and/or atmospheric pollution, heat from styling the hair and/or chemical treatment of the hair (for example curling, perming, straightening, dyeing and/or bleaching). The hair care compositions of the present invention may comprise conventional hair care products and/or specific hair protection products which may be used for example as protective pre-treatments prior to heat or chemical treatment of the hair.

25

30

35 The term "hair care composition" as used herein includes so-called "hot oil" treatments, shampoos, conditioners, hair dyes, mousses, foams, gels, creams, waxes, masks, muds, semi-solid structured styling pastes (also known as putties), styling sprays, lotions and rinses, all suitable for use on the hair of animals, preferably on human hair, most preferably hair on the human head.

- 2 -

Therefore broadly according to the present invention there is provided a hair care composition containing a combination of anti-free-radical ingredients that when combined together give a synergistic improvement in activity allowing improved protection and condition to be provided for the hair without the drawback of aesthetically unpleasant product appearance and the chance of hair staining.

The present invention provides hair care compositions containing a synergistic mixture of three anti free radical agents selected from (a) ascorbic acid, its salts and esters, particularly sodium ascorbyl phosphate, magnesium ascorbyl phosphate and ascorbyl palmitate (b) tocopherol and its esters, such as tocopherol acetate and (c) herbal extracts, particularly morus alba, such as that available under the trade name "Mulberry Concentrate" from Aston Chemicals; origanum vulgare, such as that available under the trade name "Pronalen Origanum HSC" from S Black Ltd; panax ginseng, such as that available under the trade name "Ginseng 1.1 extract 4294" from S Black Ltd; rosmarinus officinalis, such as that available under the trade name Herbal Rosemary WS from Chesham Chemicals or Pronelen Rosemary extract from S.Black Ltd; camellia sinensis such as that available under the trade name "Herbal Extract Green Tea 75% Solids" from Nichimen Europe; and grape seed extract such as that available under the trade name Grape Seed Extract WS from S.Black Ltd. In combination with a suitable diluent or carrier. The agents used in the present invention are already known for their individual ability to quench free radicals and prevent oxidative damage to the hair. However the present invention discloses that certain combinations of these agents have an efficacy much greater than expected. This has been demonstrated experimentally.

The commercially available sources of the anti-free-radical agents used in the present invention consist of the anti free-radical agents but these may also comprise diluents and/or carriers. Thus there may be some confusion as to the actual level of agent within a commercially available product. Accordingly, the amounts of anti free-radical agents used in the present invention are expressed as dry weights, as understood by a man skilled in the art.

The total amount of anti-free radical agents present in the composition may range from 0.003% to 10% by weight. Where the synergistic mixture of anti free-radical agents is comprised solely of herbal extracts, then a preferred total

- 3 -

amount of anti free-radical agents is 0.005% to 1%w/w, most preferably 0.01% to 0.6% by weight of the composition.

5 Preferably, the individual anti-free-radical agents that comprise the synergistic mixtures may be present in an amount of from about 0.001% to about 10% by weight, more preferably from about 0.003% to about 5% by weight, most preferably 0.004 to 0.2% by weight of the composition.

10 Particularly preferred synergistic combinations of anti free-radical agents suitable for inclusion in a hair care composition are:

Origanum vulgare, sodium ascorbyl phosphate and morus alba.

15 Origanum vulgare, sodium ascorbyl phosphate and panax ginseng.

Panax ginseng, morus alba and origanum vulgare.

Sodium ascorbyl phosphate, morus alba and camellia sinensis

20 Sodium ascorbyl phosphate, morus alba and grape seed

Origanum vulgare, panax ginseng and rosmarinus officinalis.

25 A hair care composition containing a synergistic combination of anti free-radical agents has a multitude of advantages. Such anti free-radical agents are usually highly coloured. If they are used individually in amounts necessary to be totally effective, it is likely that the hair care composition would stain both skin and clothes and would dye the hair. Further, even at lower levels the agents give the composition a cosmetically unacceptable appearance. Thus most conventional  
30 hair compositions use less of an anti free-radical agent than necessary to provide total protection. With the present invention because of the increased efficacy of the synergistic mixture of anti-free radical agents it is possible to include the anti free-radical agents in sufficient amounts to provide an effective defence against the action of free radicals. Thus use of the composition will give  
35 the users hair improved shine, feel, manageability, flexibility, colour and will help protect the hair from damage. All this is provided without the aforementioned disadvantages of staining, dyeing and unacceptable cosmetic appearance.

- 4 -

Alternatively, if the same level of protection as a conventional formulation is required, then the increased efficacy of the synergistic mixture of anti free-radical agents means that the composition will require much lower quantities of the anti free-radical agents than a conventional formulation. Not only are any problems with highly coloured formulations reduced (staining, dyeing, cosmetic appearance), but the cost of the formulation is likely to be cheaper as well.

To further reduce the generation of free-radicals by the UV radiation in sunlight, compositions of the present invention may further comprise any acceptable sunscreens (that is an agent which acts to absorb and/or reflect UV radiation present in sunlight) and which would be acceptable for use in a hair-care composition (for example suitable for use on the human head). Such sunscreens may comprise inorganic sunscreens (for example zinc oxide and/or titanium dioxide preferably of microfine (< 100 nm) particle size) and/or organic sunscreens (for example p-aminobenzoic acids, esters and derivatives, methoxycinnamate esters, benzophenones [such as benzophenone-4 {available commercially under the trade name Uvinul MS40}]; dibenzoylmethanes and/or salicylate esters). The sunscreens may be present in an amount of from about 0.1% to about 10% by weight of the composition.

Further components may be added to the hair care composition as is well-known to those skilled in the art.

For example, preservatives may be added to the composition such as 2-bromo-2-nitropropane-1,3-diol (bronopol, which is available commercially under the trade name Myacide RTM), benzyl alcohol, diazolidinyl urea, imidazolidinyl urea, methyl paraben, phenoxy ethanol, propyl paraben, sodium methyl paraben and sodium propyl paraben, suitably in an amount of from about 0.01% to about 10% by weight of the composition.

Thickeners and viscosity modifying agents may be added to the composition, such as amine oxides, block polymers of ethylene oxide and propylene oxide (for example, those available from BASF Wyandotte under the trade name "Pluronic" RTM), ethoxylated fatty alcohols, cellulosic derivatives such as hydroxypropylmethyl cellulose, salt (NaCl), phthalic acid amide, polyvinyl

- 5 -

alcohols and fatty alcohols, suitably in an amount of from about 0.5% to about 10% by weight of the composition.

Sequestering agents may be added to the composition, such as ethylenediamine tetraacetic acid and salts thereof, suitably in an amount of from about 0.005% to about 0.5% by weight of the composition.

The composition may also include resins such as: octylacrylamide / acrylates / butylaminomethacrylate copolymer (available under the trade name Amphomer RTM); ethyl ester of polyvinylmethyl (hereinafter known as PVM) / methylacrylate (hereinafter known as MA) copolymer (available under the trade name Ultrahold 8A RTM); vinyl acetate (hereinafter known as VA) / crotonates / vinyl neodecanate copolymer (available under the trade name Adhesive 28-2930 NAL); acrylates / acrylamide copolymer (available under the trade name Gantrez ES225 RTM); vinyl acetate / crotonic acid / vinyl propionate copolymer (available under the trade name Luviset CAP RTM); polyvinylpropionate (hereinafter known as PVP) / VA / vinylpropionate copolymer (available under the trade name Laviskol VAP RTM); octylacrylamide / acrylate copolymer (available under the trade names Versatyl 90 RTM or Lovocryl 47 RTM); vinyl caprolactam / PVP / dimethylaminoethyl methacrylate copolymer (available under the trade name (H<sub>2</sub>O LD EP-1); PVM / MA copolymer (available under the trade name Gantrez RTM); and vinyl acetate / butyl maleate / isobornyl acrylate copolymer (available under the trade name Advantage CP RTM). These resins may be present suitably in an amount of from about 0.1% to about 10% by weight of the composition.

The composition may also include slip aids such as phenyl trimethicone, suitably in an amount of from about 0.1% to about 10% by weight of the composition.

The composition may also include vitamins such as biotin, suitably in an amount of from about 0.01% to about 1.0% by weight of the composition.

The composition may also include waxes such as cocoa butter suitably in an amount of from about 1% to about 99% by weight of the composition.

The composition may also include gelling agents such as PVM, MA, or a

- 6 -

decadiene crosspolymer (available under the trade name Stabirez 06), suitably in an amount of from about 0.1% to about 2% by weight of the composition.

5 The composition may also comprise suitable, cosmetically acceptable diluents, carriers and/or propellants such as dimethyl ether.

10 The composition may also include pearlising agents such as stearic monoethanolamide, suitably in an amount of from about 0.01% to about 10% by weight of the composition.

15 Perfumes may be added suitably in an amount of from about 0.01% to about 2% by weight of the composition, as may water soluble dyes such as tartrazine, suitably in an amount of from about a trace amount (such as  $1 \times 10^{-5}$  %) to about 0.1% by weight of the composition.

20 The composition may also include pH adjusting agents such as sodium hydroxide, aminomethyl propanol, triethanolamine, suitably in an amount of from about 0.01% to about 10% by weight of the composition.

25 The composition may be buffered by means well known in the art, for example by use of buffer systems comprising succinic acid, citric acid, lactic acid, and acceptable salts thereof, phosphoric acid, mono- or disodium phosphate and sodium carbonate. Suitably, the composition may have a pH between about 3 and about 10, preferably between about 4 and about 8.

30 The composition may also include an antidandruff agent such as salicylic acid or zinc pyrithione or octopyrox suitably in an amount of from about 0.1% to about 5% by weight of the composition.

35 Surfactants may be included, such as cosmetically acceptable salts of alkyl ether sulphates, alkyl and alkylamidoalkyl betaines, ethoxylated alcohols, polyethyleneglycol carboxylates, acceptable salts of alkyl sulphates (such as ammonium lauryl sulphate), acceptable salts of alkyl ether sulphates (such as ammonium laureth sulphate or sodium laureth sulphate ), sulphosuccinates (such as disodium laureth sulphosuccinate), amphotacetates and amphodiactates (such as disodium cocoamphodiactate), alkylpolyglucosides and alcohol sulphonates.

- 7 -

In accordance with a further aspect of the present invention there is provided a method of treating hair (for example washing, conditioning and/or styling hair) by application to the hair of a composition as described herein.

5

The invention will be illustrated with reference to the non-limiting tests and formulation examples described hereinafter:

**Example 1 - Hair Conditioner**

10

Ingredients	%W/W
Aqua	to 100
Cetyl alcohol	3
15 Cetrimonium chloride	0.759
Hydroxyethylcellulose	0.6
Propylene glycol	0.493
Panthenol	0.375
Parfum	0.3
20 Benzophenone-4	0.2
Sodium chloride	0.15
Wheat amino acids	0.14
Amodimethicone	0.105
Alcohol denat.	0.095
25 Dimethicone propyl PG-betaine	0.09
Citric acid	0.026
Tetrasodium EDTA	0.02
Trideceth-10	0.0045
Origanum vulgare	0.009
30 Panax ginseng	0.006
Morus alba	0.0046

35

The EDTA and hydroxyethylcellulose were added to the water and mixed using a homogeniser to hydrate the polymer. Citric acid, benzophenone and cetrimonium chloride were added. This was then heated to 70°C.



- 8 -

Cetyl alcohol was heated to 70°C in a separate vessel and was then added to the aqueous mixture using a homogeniser. The mixture was then cooled to below 40°C using a propeller stirrer. The remaining materials including the antioxidant complex were then added and the product was made to weight with purified water.

### **Example 2 - Intensive Conditioner**

	Ingredients	%W/W
10	Aqua	to 100
	Cetearyl alcohol	4.6
	Arachidyl propionate	2
	Dimethicone	2
15	Panthenol	1.5
	Stearamidopropyl dimethylamine	1.5
	Hydroxyethylcellulose	0.75
	Amodimethicone	0.7
	Citric acid	0.503
20	Cetrimonium chloride	0.435
	PEG-20 stearate	0.4
	Parfum	0.3
	Propylene glycol	0.29
	Benzophenone-4	0.2
25	Sodium chloride	0.15
	Wheat amino acids	0.14
	Polyquaternium-39	0.1
	Alcohol denat.	0.095
	Trideceth-10	0.03
30	BHT	0.025
	Isopropyl alcohol	0.02
	Tetrasodium EDTA	0.02
	Origanum vulgare	0.009
	Panax ginseng	0.006
35	Morus alba	0.0046

The EDTA and hydroxyethylcellulose were added to the water and mixed using

- 9 -

a homogeniser to hydrate the polymer. The citric acid and cetrimonium chloride were added and mixed using a propeller stirrer. The mixture was then heated to 70°C. In a separate vessel, the waxes, dimethicone and BHT were mixed and heated to 70°C until melted and uniform. This mixture was then added to the aqueous mixture and this was mixed until uniform. The resulting mixture was then cooled to below 40°C with stirring and the remaining materials including the antioxidant complex were then added and the product was made to weight using purified water.

### 10 Example 3 - Leave In Conditioner

	Ingredients	%WW
	Aqua	to 100
15	PEG-40 hydrogenated castor oil	2
	Dipropylene glycol	1
	Phenoxyethanol	0.85
	Parfum	0.4
	Panthenol	0.375
20	Propylene glycol	0.29
	Methylparaben	0.2
	Benzophenone-4	0.2
	Alcohol denat.	0.095
	Polyquaternium-10	0.091
25	Sodium chloride	0.3
	Wheat amino acids	0.028
	Sodium hydroxide	0.026
	Origanum vulgare	0.009
	Panax ginseng	0.006
30	Morus alba	0.0046

The polyquaternium-10 was added to the water and hydrated using a propeller stirrer. The methylparaben was pre-dispersed in the dipropylene glycol, gently heated to melt and then added to the hydrated polyquaternium-10 mixture. The remaining materials including the antioxidant complex were then added and the product was mixed and made to weight with purified water.

- 10 -

**Example 4 - Gentle Shampoo**

	Ingredients	%W/W
5	Aqua	to 100
	Sodium laureth sulfate	8.25
	Cocamidopropyl betaine	2.8
	Sodium chloride	1.794
	Cocamide DEA	1.63
10	PEG-6 cocamide	1
	Parfum	0.5
	Panthenol	0.375
	Propylene glycol	0.29
	Benzophenone-4	0.2
15	Glycerin	0.2
	Phenoxyethanol	0.162
	Wheat amino acids	0.14
	Alcohol denat.	0.095
	Citric acid	0.05
20	Methyldibromo glutaronitrile	0.04
	Tetrasodium EDTA	0.02
	Origanum vulgare	0.009
	Panax ginseng	0.006
	Morus alba	0.0046
25		

EDTA, sodium chloride, citric acid and benzophenone-4 were added to the water. This was followed by the addition of sodium laureth sulfate, methyldibromo glutaronitrile, wheat amino acids and the antioxidant complex.

30 PEG-6 cocamide and cocamide DEA were heated gently until liquified. The parfum was added and mixed. This was then added to the above mixture. The cocamidopropyl betaine and remaining materials were then added and mixed. The product was made to weight using purified water.

- 11 -

**Example 5 - Anti-Dandruff Shampoo**

	Ingredients	%W/W
5	Aqua	to 100
	Sodium laureth sulfate	5.9
	Disodium laureth sulfosuccinate	4
	Laureth-3	3
	Cocamidopropyl betaine	2.45
10	Sodium chloride	1.926
	Dipropylene glycol	1
	Parfum	0.5
	Piroctone olamine	0.5
	Panthenol	0.375
15	Propylene glycol	0.29
	Disodium phosphate	0.25
	Benzophenone-4	0.2
	Wheat amino acids	0.14
	Alcohol denat.	0.095
20	Citric acid	0.063
	Tetrasodium EDTA	0.02
	Preservative	0.2
	Origanum vulgare	0.009
	Panax ginseng	0.006
25	Morus alba	0.0046

EDTA, citric acid and benzophenone-4 were mixed into the water. Sodium laureth sulfate, disodium laureth sulfosuccinate, dipropylene glycol, disodium phosphate, wheat amino acids and the antioxidant complex were added and the product was stirred until uniform. The piroctone olamine was dispersed in the parfum and added to the laureth-3. This mixture was added to the bulk and stirred. The remaining materials were then added and the product was made to weight with purified water.

- 12 -

**Example 6 - Anti-Chlorine Shampoo**

	Ingredients	%W/W
5	Aqua	to 100
	Sodium laureth sulfate	7.6
	Cocamidopropyl betaine	2.8
	Sodium chloride	1.694
	Laureth-3	1
10	Phenoxyethanol	0.852
	Parfum	0.5
	Disodium phosphate	0.4
	Panthenol	0.375
	Propylene glycol	0.29
15	Methylparaben	0.2
	Benzophenone-4	0.2
	Wheat amino acids	0.14
	Propylparaben	0.1
	Sodium thiosulfate	0.1
20	Alcohol denat.	0.095
	Sodium hydroxide	0.06
	Sodium phosphate	0.06
	Tetrasodium EDTA	0.02
	Origanum vulgare	0.009
25	Panax ginseng	0.006
	Morus alba	0.0046

30 Benzophenone, sodium chloride, sodium phosphate, disodium phosphate and EDTA were added to the water and mixed. Sodium laureth sulfate, phenoxyethanol, panthenol, wheat amino acids and the antioxidant complex were then added and stirred. The preservatives were pre-mixed in the laureth-3 and heated slightly to melt the powders. This was added to the product. The remaining materials were added and the product was made to weight using

35 purified water.

- 13 -

**Example 7 - Hair Gel**

	Ingredients	%WW
5	Aqua	to 100
	Cyclomethicone	6.6
	Dimethiconol	0.9
	Phenoxyethanol	0.8
	Propylene glycol	0.79
10	Panthenol	0.75
	Carbomer	0.7
	Aminomethyl propanol	0.4
	Benzophenone-4	0.2
	Parfum	0.2
15	Alcohol denat.	0.095
	Tetrasodium EDTA	0.05
	Sodium chloride	0.03
	Wheat amino acids	0.028
	Origanum vulgare	0.009
20	Panax ginseng	0.006
	Morus alba	0.0046

EDTA and benzophenone-4 were added to the water using an homogeniser. The carbomer was added and hydrated with continued homogenising. The phenoxyethanol, cyclomethicone, dimethiconol, propylene glycol and panthenol were then added and mixed until homogenous. The remaining materials including the antioxidant complex were added and the bulk was homogenised until uniform and the product was made to weight using purified water.

**Example 8 - Semi-solid Structured Styling Paste for Hair**

This type of product is also known as a hair putty

	Ingredients	%WW
35	Aqua	to 100
	Cetearyl alcohol	10.9

- 14 -

	Lanolin	7
	PVP	6
	Paraffin	6
	PVP/VA copolymer	5.7
5	Carnauba	3
	Petrolatum	2
	Polyquaternium-11	2
	PEG-20 stearate	1.9
	Paraffinum liquidum	1
10	Propylene glycol	0.8
	Phenoxyethanol	0.6
	Dimethicone	0.5
	Panthenol	0.375
	Cetrimonium chloride	0.35
15	Dimethicone propyl PG-betaine	0.225
	Benzophenone-4	0.2
	Methylparaben	0.12
	Alcohol denat.	0.095
	Origanum vulgare	0.009
20	Panax ginseng	0.006
	Morus alba	0.0046

The PVP/VA copolymer, PVP and benzophenone-4 were added to the water and stirred until homogenous. This was then heated to 70°C. In a separate vessel, the waxes were mixed and heated to 70°C until all materials had melted. The hot waxes were then added to the aqueous mixture and mixed using a propeller stirrer until homogenous. The mixture was then cooled to below 60°C and the remaining materials, including the antioxidant complex were then added and the product was stirred until uniform. The product was made to weight using purified water.

#### Example 9 - Moisturising Conditioner

	Ingredients	%W/W
35	Aqua	to 100
	Cetyl alcohol	4

- 15 -

	Dimethicone	2
	Hydroxyethylcellulose	0.8
	Cetrimonium chloride	0.765
	Panthenol	0.75
5	Propylene glycol	0.64
	Parfum	0.3
	Benzophenone-4	0.2
	Amodimethicone	0.175
	Dimethicone propyl PG-betaine	0.15
10	Sodium chloride	0.15
	Wheat amino acids	0.14
	Alcohol denat.	0.095
	Citric acid	0.026
	Tetrasodium EDTA	0.02
15	Trideceth-10	0.009
	Origanum vulgare	0.009
	Panax ginseng	0.006
	Morus alba	0.0046
20	EDTA and hydroxyethylcellulose were added to the water using homogenising to hydrate the polymer. The benzophenone-4 and Laureth-3 were then added and the bulk was heated to 70°C. In a separate vessel, the cetyl alcohol was heated to 70°C until melted and was then added to the bulk and mixed with a homogeniser until uniform. The product was cooled and the remaining	
25	materials, including the antioxidant complex were then added and mixed. The product was made to weight using purified water.	

**Example 10 - Spray Gel**

30	Ingredients	%W/W
	Phase 1	
35	Aqua	to 100
	PVP/VA copolymer	4.9
	Isopropyl alcohol	2.5



- 16 -

	Propylene glycol	2.29
	Glycerin	2
	Panthenol	0.375
	Benzophenone-4	0.2
5	Sodium chloride	0.03
	Wheat amino acids	0.028
	Origanum vulgare	0.009
	Panax ginseng	0.006
	Morus alba	0.0046
10	Phase 2	
	PEG-40 hydrogenated castor oil	1
	Parfum	0.3
15	Phase 3	
	Alcohol denat.	45
	Dimethicone copolyol	1
20		

The materials in phase 1 were mixed until uniform using a propeller stirrer. The materials in phase 2 were pre-mixed and added to phase 1. The materials in phase 3 were mixed and added to the bulk. The product was made to weight using purified water.

#### Example 11 - Dry Scalp Shampoo

30	Ingredients	%W/W
	Aqua	to 100
	Sodium laureth sulfate	7
	Sodium chloride	2.23
35	Cocamidopropyl betaine	1.96
	Laureth-3	1
	Panthenol	0.375

- 17 -

	Propylene glycol	0.29
	Piroctone olamine	0.25
	Benzophenone-4	0.2
	Phenoxyethanol	0.162
5	Wheat amino acids	0.14
	Polyquaternium-39	0.1
	Alcohol denat.	0.095
	Citric acid	0.06
	Methyldibromo glutaronitrile	0.04
10	Tetrasodium EDTA	0.02
	Origanum vulgare	0.009
	Panax ginseng	0.006
	Morus alba	0.0046
15	EDTA, citric acid, benzophenone-4 and sodium chloride were added and mixed using a propeller stirrer until all materials were dissolved and uniform. The sodium laureth sulfate and piroctone olamine were then added and stirred until homogenous. The remaining materials, including the antioxidant complex were then added and the product was stirred until uniform and homogenous. The	
20	product was made to weight with purified water.	

**Example 12 - Deep Cleaning Shampoo**

25	Ingredients	%W/W
	Aqua	to 100
	Sodium laureth sulfate	14.13
	Sodium chloride	2.72
30	Cocamidopropyl betaine	1.4
	PEG-6 cocamide	1
	Parfum	0.5
	Panthenol	0.375
	Propylene glycol	0.29
35	Benzophenone-4	0.2
	Phenoxyethanol	0.162
	Wheat amino acids	0.14

- 18 -

	Alcohol denat.	0.095
	Methyldibromo glutaronitrile	0.04
	Citric acid	0.02
	Tetrasodium EDTA	0.02
5	Origanum vulgare	0.009
	Panax ginseng	0.006
	Morus alba	0.0046

10 Citric acid, EDTA and sodium chloride were added to the water and dissolved.  
 The benzophenone-4, sodium laureth sulfate, cocamidopropyl betaine, panthenol, methyldibromo glutaronitrile, wheat amino acids and the antioxidant complex were then added and mixed until the product was uniform, using a propeller stirrer. The parfum was pre-dispersed in the PEG-6 cocamide and then added to the bulk. The product was made to weight using purified water.

15

### Example 13 - Moisturising Shampoo

	Ingredients	%W/W
20	Aqua	to 100
	Sodium laureth sulfate	8.24
	Cocamidopropyl betaine	2.8
	Cocamide DEA	1.63
25	Panthenol	1.5
	Sodium chloride	1.5
	Laureth-3	1.194
	Parfum	0.5
	Propylene glycol	0.5
30	Polyquaternium-10	0.273
	Glycerin	0.2
	Wheat amino acids	0.14
	Alcohol denat.	0.095
	Dimethicone propyl PG-betaine	0.09
35	Citric acid	0.04
	Tetrasodium EDTA	0.02
	Origanum vulgare	0.009

- 19 -

Panax ginseng	0.006
Morus alba	0.0046

EDTA and polyquaternium-10 were added to the water and the polymer was hydrated using an homogeniser. The citric acid, sodium chloride and benzophenone-4 were added and stirred until uniform. The remaining materials, including the antioxidant complex were added individually and the product was mixed using a propeller stirrer until homogenous. The product was made to weight using purified water.

#### Example 14 - Extra Hold Hair Gel

	Ingredients	%W/W
15	Aqua	to 100
	PVP/VA copolymer	1.9
	Propylene glycol	1.29
	Carbomer	1
	PEG-40 hydrogenated castor oil	1
20	Panthenol	0.375
	Sodium hydroxide	0.26
	Parfum	0.2
	Phenoxyethanol	0.16
	Tetrasodium EDTA	0.15
25	Mica	0.113
	Cystine hydroxypropyl polysiloxane	0.1
	Alcohol denat.	0.095
	Methyldibromo glutaronitrile	0.04
	Sodium chloride	0.03
30	Wheat amino acids	0.028
	Benzophenone-2	0.025
	Origanum vulgare	0.009
	Panax ginseng	0.006
	Morus alba	0.0046
35	Method	

EDTA, methyldibromo glutaronitrile, PVP/VA copolymer and carbomer were

- 20 -

added to the water and mixed using a homogeniser to ensure that the polymers were hydrated. With continued homogenising, the cystine hydroxypropyl polysiloxane was added and mixed into the product. The remaining materials, including the antioxidant complex were added individually and mixed using a propeller stirrer until the product was homogenous.

#### Example 15 - Gentle Shampoo

	Ingredients	%W/W
10	Aqua	to 100
	Sodium laureth sulfate	8.25
	Cocamidopropyl betaine	2.8
	Sodium chloride	1.794
15	Cocamide DEA	1.63
	PEG-6 cocamide	1
	Parfum	0.5
	Panthenol	0.375
	Propylene glycol	0.29
20	Benzophenone-4	0.2
	Glycerin	0.2
	Phenoxyethanol	0.162
	Wheat amino acids	0.14
	Alcohol denat.	0.095
25	Citric acid	0.05
	Methyldibromo glutaronitrile	0.04
	Tetrasodium EDTA	0.02
	Origanum vulgare	0.2
	Panax ginseng	0.2
30	Morus alba	0.2

EDTA, sodium chloride, citric acid and benzophenone-4 were added to the water. This was followed by the addition of sodium laureth sulfate, methyldibromo glutaronitrile, wheat amino acids and the antioxidant complex. PEG-6 cocamide and cocamide DEA were heated gently until liquified. The parfum was added and mixed. This was then added to the above mixture. The

- 21 -

cocamidopropyl betaine and remaining materials were then added and mixed. The product was made to weight using purified water.

### **Example 16 - Gentle Shampoo**

5	Ingredients	%W/W
	Aqua	to 100
	Sodium laureth sulfate	8.25
10	Cocamidopropyl betaine	2.8
	Sodium chloride	1.794
	Cocamide DEA	1.63
	PEG-6 cocamide	1
	Parfum	0.5
15	Panthenol	0.375
	Propylene glycol	0.29
	Benzophenone-4	0.2
	Glycerin	0.2
	Phenoxyethanol	0.162
20	Wheat amino acids	0.14
	Alcohol denat.	0.095
	Citric acid	0.05
	Methyldibromo glutaronitrile	0.04
	Tetrasodium EDTA	0.02
25	Origanum vulgare	0.2
	Panax ginseng	0.2
	Rosmarinus officinalis	0.2

30 EDTA, sodium chloride, citric acid and benzophenone-4 were added to the water. This was followed by the addition of sodium laureth sulfate, methyldibromo glutaronitrile, wheat amino acids and the antioxidant complex. PEG-6 cocamide and cocamide DEA were heated gently until liquified. The parfum was added and mixed. This was then added to the above mixture. The  
 35 cocamidopropyl betaine and remaining materials were then added and mixed. The product was made to weight using purified water.

A number of trials were conducted to demonstrate the efficacy of the synergistic combinations of anti-free radical agents.

5

### *In Vitro* Tests

10

Linoleic acid (model skin and hair lipid) was incubated in the presence of various antioxidants and antioxidant combinations and was exposed to broad spectrum UVA/B to induce oxidation of the lipid. Following extraction of the lipid into methanol, the amount of lipid hydroperoxides (free radical generated damage) formed were measured with a specific colorimetric biochemical test. The degree of inhibition afforded by the antioxidants was thus measured and compared to irradiated vehicle controls.

15

The percentage inhibition of free radical mediated lipid peroxidation when compared to the vehicle alone are given below.

	<u>Antioxidants</u>	<u>% inhibition</u>
20	Morus alba (ma)	0
	Origanum vulgare (ov)	49
	Panax ginseng (pg)	5.7
	Sodium ascorbyl phosphate (nap)	21
	Grape seed (gs)	0
25	Camellia sinensis (cc)	19
	Observed effect of nap/pg/ov	100
	Predicted effect of nap/pg/ov	75.7
30	Observed effect of nap/ma/ov	100
	Predicted effect of nap/ma/ov	70
	Observed effect of nap/ma/cc	100
	Predicted effect of nap/ma/cc	40
35	Observed effect of nap/ma/gs	81
	Predicted effect of nap/ma/gs	21

- 23 -

Thus it can be seen that the observed inhibiting effect of using the above combinations of antioxidants is greater than that which would be expected from the sum of the contributions of the individual thus demonstrating a synergistic effect.

In a second series of experiments using antioxidants collected in a later season gave the following results.

	<u>Antioxidant</u>	<u>% inhibition</u>
	morus alba (ma)	37
	origanum vulgare (ov)	29
	rosmarinus officinalis (ro)	15
	panax ginseng (pg)	10
	Observed effect of ro/pg/ov	88
	Predicted effect of ro/pg/ov	54
	Observed effect of pg/ma/ov	93
	Predicted effect of pg/ma/ov	76

Thus it can be seen that the observed inhibiting effect of using the above combinations of antioxidants is greater than that which would be expected from the sum of the contributions of the individual thus demonstrating a synergistic effect.

### *In Vivo Tests*

Swatches of hair were tied at each end and then cut into two pieces. One of these pieces was used as a test and the other was used as a control. Each piece was washed with either the shampoo under test or a control containing no anti-free-radical agents for one minute and then rinsed in tepid water for 30 seconds. The swatches were then fixed on a plate and irradiated with broad spectrum UVA/B light for 8 hours in the Heredus Suntest plus to induce oxidation of the lipid. Samples of each swatch (0.12 g) were weighed out and placed in an epindorph tube. A 2:1 mixture of chloroform and methanol (1 m) was added. The tubes were placed in a centrifuge tube, placed on a tumbula



- 24 -

5 mixer and mixed for 2 hours in a refrigerator. The hair was removed and the solvent removed under nitrogen. The lipids were resolubilised by adding methanol (50 µl) and vortexing for 15 seconds. Aliquots (7.5 µl) were plated out in triplicate and assayed for the level of oxidised lipid using a commercially available specific colourimetric biochemical test (K-Assay LPO kit). Each test was repeated with 5 separate hair swatches and the mean result for each of the 3 determinations for all five swatches enabled the amount of oxidised lipid to be measured.

10 The composition of Example 1 containing morus alba (0.2%), origanum vulgare (0.2%) and panax ginseng (0.2%) showed an amount of oxidised lipid of 113 nmol/ml compared to 181 nmol/ml for the control. The reduction in the amount of oxidised lipid is therefore around 38%.

15 The composition of Example 8 containing morus alba (0.2%), origanum vulgare (0.2%) and panax ginseng (0.2%) showed an amount of oxidised lipid of 372 nmol/ml compared to 553 nmol/ml for the control. The reduction in the amount of oxidised lipid is therefore around 33%.

20 The composition of Example 15 containing morus alba (0.2%), origanum vulgare (0.2%) and panax ginseng (0.2%) showed an amount of oxidised lipid of 482 nmol/ml compared to 731 nmol/ml for the control. The reduction in the amount of oxidised lipid was around 34%.

25 The composition of Example 16 containing rosmarinus officinalis (0.2%), origanum vulgare (0.2%) and panax ginseng (0.2%) showed an amount of oxidised lipid of 601 nmol/ml compared to 694 nmol/ml for the control. The reduction in the amount of oxidised lipid was around 13%.

### Sensory analysis

35 Swatches of hair treated with either base formulation or formulations containing antioxidants were assessed by an expert panel for factors such as shine, softness, static, ease of combing, gloss and overall feel. Statistical analysis was used to determine whether antioxidants were able to protect and enhance

- 25 -

these properties.

The results showed an improvement in shine and feel.

- 26 -

**CLAIMS**

1. Hair care compositions containing a synergistic mixture of three anti-free-radical agents selected from

(a) ascorbic acid, its salts and esters;

(b) tocopherol and its esters, such as tocopherol acetate; and

(c) herbal extracts selected from morus alba, organum vulgare, panax ginseng, rosmarinus officinalis, camellia sinensis and grape seed extract

in a suitable diluent or carrier.

2. Hair care compositions as claimed in claim 1 wherein the esters of ascorbic acid are sodium ascorbyl phosphate, magnesium ascorbyl phosphate, magnesium ascorbyl phosphate or magnesium ascorbyl palmitate.

3. Hair care compositions as claimed in claim 1 or claim 2 wherein the total amount of anti-free-radical agents present lies in the range 0.003 to 10% by weight.

4. Hair care compositions as claimed in any preceding claim wherein the total amount of anti-free-radical agents present lies in the range 0.005 to 1% by weight.

5. Hair care compositions as claimed in any preceding claim wherein the total amount of anti-free-radical agents present lies in the range 0.01 to 0.6%.

6. Hair care compositions as claimed in any preceding claims where the synergistic combination of anti-free-radicals is:

Origanum vulgare, sodium ascorbyl phosphate and morus alba.

Origanum vulgare, sodium ascorbyl phosphate and panax ginseng.

Panax ginseng, morus alba and organum vulgare.

Sodium ascorbyl phosphate, morus alba and camellia sinensis

Sodium ascorbyl phosphate, morus alba and grape seed

Origanum vulgare, panax ginseng and rosmarinus officinalis.

- 27 -

7. A method of treating hair which comprises the application to the hair of a hair care composition as claimed in any one of claims 1 to 6.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 00/07196

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 A61K7/06

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98 42309 A (W. CRANDALL ) 1 October 1998 (1998-10-01) example 9	1
X	DE 42 27 806 A (FISCHER PHARMACEUTICALS LTD) 25 February 1993 (1993-02-25) example 17	1
X	FR 2 746 008 A (J-N. THOREL) 19 September 1997 (1997-09-19) example 5	1
P, X	US 6 066 327 A (J. GUBERNICK ET AL.) 23 May 2000 (2000-05-23) the whole document	1
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*Z\* document member of the same patent family

Date of the actual completion of the international search

30 November 2000

Date of mailing of the international search report

12/12/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040. Tx. 31 651 epo nl.  
Fax: (+31-70) 340-3016

Authorized officer

Glikman, J-F

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 00/07196

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 102 659 A (T. HUDSON) 7 April 1992 (1992-04-07) the whole document ---	1
X,P	US 5 962 517 A (H. MURAD) 5 October 1999 (1999-10-05) example 3 ---	1
X	DATABASE WPI Week 9727 Derwent Publications Ltd., London, GB; AN 1997-295529 XP002154265 & JP 09 111237 A (HASEQYWA CO., LTD), 28 April 1997 (1997-04-28) abstract -----	1

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat'l Application No

PCT/EP 00/07196

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9842309 A	01-10-1998	US 5945409 A AU 6775098 A	31-08-1999 20-10-1998
DE 4227806 A	25-02-1993	IL 99291 A AU 654030 B AU 2122092 A CA 2076467 A CH 684739 A ES 2050074 A FR 2680466 A GB 2259014 A,B PT 100800 A,B	15-04-1997 20-10-1994 25-02-1993 24-02-1993 15-12-1994 01-05-1994 26-02-1993 03-03-1993 28-02-1994
FR 2746008 A	19-09-1997	NONE	
US 6066327 A	23-05-2000	US 6068848 A AU 1830199 A EP 0967969 A WO 9930682 A	30-05-2000 05-07-1999 05-01-2000 24-06-1999
US 5102659 A	07-04-1992	CA 2046964 A GB 2245812 A,B JP 4226588 A MX 9100199 A	13-01-1992 15-01-1992 17-08-1992 28-02-1992
US 5962517 A	05-10-1999	NONE	
JP 09111237 A	28-04-1997	NONE	